VOL. XXIII. [FEBRUARY, 1901.] NO. 2.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE CONDITION, PROSPECTS, AND FUTURE EDUCATIONAL DEMANDS OF THE CHEMICAL INDUSTRIES.[1]

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Received January 8, 900.

IT has been well said that chemistry is an offspring of the nineteenth century. The closing years of the eighteenth century had some glimpses of the wonders the new science had in store, but it remained for the workers of the first decade of the nineteenth to collaborate the results obtained by their immediate predecessors and develop the new truths which finally established the foundation of the glorious structure, which has now grown so great. . During this period, human necessities were in every way augmented and particularly in France, claimed to be the fatherland of our science, human ingenuity was sorely taxed to meet these needs.

The struggle to find ways and means stimulated the energies and increased the zeal of the searchers after truth, and the utilitarian quest, as is always inevitable, brought forth results of interest and value above and beyond the actual needs, furnished data upon which are based the most important and fundamental laws of the science, and firmly established many of the most important of our industries. The labors of the chemists of the

[1] Presidential address delivered at the Chicago meeting of the American Chemical Society, December 27, 1900.

last decade of the closing century had cleared away the haze which surrounded and covered the truths already developed and opened the way for further promotion of the newly born science. Lavoisier had led by the introduction of systematic and accurate observation and record, to the crystallization of what had so far concentrated, and his associates, imbued with his spirit and inspired by his genius, were ready and willing to carry forward what he had so nobly begun.

And so the science was launched. How it has progressed during the century now closing has been told in many ways by many men and the history seems ever new. New laws and new truths found applications in the industries and increased the material wealth and the industries in turn furnished the material, the data, the incentive, for much of the additional investigation necessary to the development of the further laws.

The activity of the last decade of the last century has its counterpart in that of the century just closing. If the former century established the foundations, the closing century has furnished a superstructure worthy of the great minds who began the work. And whether we consider the later achievements from the side of abstract science or from that of the applications of the great laws to the material needs the glory is equally manifest and the wonder no less profound. Whether we consider argon and helium, neon, krypton, and xenon, and the beautiful researches which led to their discovery, polonium and radium, and their remarkable properties, the Roentgen reactions or the liquefied gases, and the attainment of the almost lowest limit of low temperatures, or the wonderful advances in illumination, the production of high temperatures in the electric furnace, the development of new compounds and forms of matter through the aid of these temperatures, the applications of high electric tensions to the production of new reactions, even those most familiar with them must feel the influence of the mighty strides and look into the future with enthusiastic hope.

The interest manifested in the new science in the old world was quickly extended to the new and it found most active lodgment here. Students and associates of Black in Scotland, Fothergill in England, and of the French chemists of the last quarter of the century in Paris, started the work and the names of Rush, Hutch-

inson, Woodhouse, McLean, Franklin, Rumford, Priestley, Silliman, Hare, Seybert, Norton, Dana, and others, will ever find affectionate memories in the minds of the chemists of America. What these men started has been actively developed by those who followed them, until to-day the science and its applications find more actual workers in our country than is to be found in any other country within the bounds of civilization.

The first half of the century had comparatively few men in the United States who could be classed as working chemists. Chemistry had, it is true, been taught in a way in many of the colleges. But systematic work, as we know it to-day in many of the institutions of learning, was practically unknown. Those who felt the special need of, and had a desire for, such instruction, were constrained to seek the facilities in other lands, until generous and at the same time practical men, such as Lawrence, Sheffield, Packer, Pardee, and Harrison, with enterprising eyes and prophetic vision, saw the advantages to be derived from the further development of the sciences and provided the means whereby well furnished laboratories could be opened up and facilities for the profound study of the science could be made possible. But the industrial needs of the country for more exact knowledge of the natural laws extended beyond private munificence and the national legislatures early recognized the importance of the better education of those who must manage the rapidly growing industries. The successful efforts of the late Senator Justin S. Morrill and his associates in securing the enactment of the law, which provided for the establishment in each state of an institution for study of agriculture and the mechanic arts, is well known and will always be gratefully remembered. No less important were the efforts of the late Mr. Hatch, of Missouri, who labored so earnestly and eventually so successfully for the establishment of the state agricultural experiment stations. There can be no question that nothing has done more for the promotion of the science of chemistry and its applications than the acts of these great captains of industry and legislation. We shall not forget further the wonderful benefactions of Johns Hopkins, Clark, Case, Rose, Rockefeller, Stanford, Schermerhorn, Havemeyer, Fayerweather, Carnegie, and others, who have furnished, through splendid

munificence, the magnificent facilities not only for instruction in the science but for abstract research as well.

The science received splendid impulse and inspiration in the meeting at the grave of Priestley, in 1874. It brought the chemists of the country, then comparatively few in number, together and established the bond of good fellowship and scientific sympathy, always so necessary to true progress. The most important outcome of this most important gathering was the organization of our own Society. In his address delivered at that meeting, Professor Benjamin Silliman named 85 chemists who had contributed to the advancement of the science in the United States at that time.

In 1876, the American Chemical Society was organized and during the year enrolled 230 members, of whom 190 were professional chemists. The impulse given in Northumberland was effective, the example of a few devoted and public-spirited men was followed, and though a period of almost fifteen years was requisite to the ultimate firm establishment of the work of the organization and the integrity of the Society itself, the great aims of its founders to secure the harmonious and thorough organization of all the chemists of the country finally prevailed. The Society has continued to increase in membership and influence, until at the present time thirteen local sections have been established in various parts of the country all actively working, and at least six of them holding monthly meetings during all but the summer months, for such scientific intercourse and discussion as cannot fail to be fruitful in the promotion of the science. The roll of membership now contains about 1750 names and while this represents but a small proportion of the working chemists of the country, its growth henceforward must be rapid and the hope of the founders fairly realized.

The Journal covers, annually, nearly 1000 pages of matter fairly representative of the work of American chemists and it has become necessary because of increased demands for it to publish an edition of 2700 copies. Its pages are open to communications on all subjects relating to chemistry and its applications, and it is the hope and expectation that the valuable Review of American Chemical Research may be accompanied in the near future by abstracts of papers published in the foreign journals, thus furnish-

ing to all our members information regarding the world's work in chemical science and practice.

The progress made in the applications of chemistry in our country can properly and fully be told only in the results of the census now in progress and in hands which promise results of higher value than have ever before been obtained in such work in this country. We may congratulate ourselves that it has been entrusted to our past president, Dr. C. E. Munroe, whose tastes and training have so admirably fitted him for the delicate and difficult task submitted to him. But we have in the figures prepared by the Bureau of Statistics of the United States Treasury most significant data regarding the progress made during this closing decade of the closing century. From this source we learn that of products classified as chemicals, drugs, and medicines, we imported during the year ending June 30, 1890, to the value of $41,601,978, while for the year ending June 30, 1900 this value had become $52,931,055. Most of the materials represented in these figures entered into consumption in industries, based wholly or in part upon the applications of chemistry. We cannot enter into the details of these statistics, but we may consider with interest and profit a few figures relating to some well-known industries and which are instructive in this connection, as showing the variations which have occurred during the decade.

CHEMICALS IMPORTED IN 1890 AND 1900 RESPECTIVELY:

	1890.	1900.
Caustic soda	$1,470,335	$ 158,793
Soda ash	3,493,288	665,104
Potash, chlorate of	238,840	102,337
Soda, chlorate of	.....	93,076
Lime, chloride of	1,385,080	1,461,858
Glycerine	928,935	2,138,670
Alizarine colors	358,882	771,336
Coal-tar colors and dyes	1,787,553	4,792,103
Other coal-tar products	.....	397,780
Milk, sugar of	46,510	399
Glass	7,411,343	4,038,753

The figures indicate enormous growth of the alkali industry in the United States during the decade and show that in this branch of industry we are entirely independent as regards supplies of foreign producers. The figures for glycerine show the possibilities

of expansion of another industry, while the almost astounding growth of the importations of alizarine and coal-tar products and dyes indicate the necessity for the further development and utilization of our own sources of crude materials of like character and the extension of that already begun. The rapid growth of the establishment of the by-product coke ovens reveals great possibilities in this direction and it must be disappointing if the characteristic enterprise fails to take advantage of these possibilities.

If the importations of chemical products are interesting and indicate great activity and growth in the industry, the figures for the exportation of similar products are even more significant. We submit figures for the years ending June 30, 1890 and June 30, 1900 respectively, including in the table some data for 1876, the year of the organization of our Society. To have predicted these results in the beginning of the quarter century would have invited incredulity, but so also would predictions regarding the advances to be made in other lines of human industry. The figures are worthy of careful study.

VALUES OF EXPORTS OF DOMESTIC PRODUCTS OF THE CHEMICAL INDUSTRIES FOR THE YEARS ENDING JUNE 30, 1876, JUNE 30, 1890, AND JUNE 30, 1900 RESPECTIVELY:

	1876.	1890.	1900.
Bark and extracts for tanning	$ 223,276	$ 263,754	$ 376,742
Beeswax	.....	17,927	91,913
Blacking	81,401	238,391	880,049
Candles	229,311	143,073	191,687
Celluloid	.....	39,004	174,264
Acids	50,300	98,084	146,722
Ashes, pot and pearl	75,597	26,211	49,566
Copper, sulphate of	.....	.....	2,120,745
Dyes and dyestuffs	.....	717,128	498,056
Lime, acetate of	.....	.....	776,413
Other chemicals not separately enumerated	2,471,195	2,840,931	5,536,716
Cider	.....	193,283	64,283
Coke	.....	53,586	1,233,921
Coffee and cocoa, ground and prepared, and chocolate	.....	93,735	228,241
Earthen-, stone-, and chinaware	.....	175,477	575,823
Fertilizers	922,221	1,618,681	7,218,224
Glass and glassware	646,954	882,677	1,933,201
Glucose or grape-sugar	.....	855,176	3,600,139
Glue	5,798	88,484	225,844

	1876.	1890.	1900.
Grease, grease scraps, and soap stock	.....	1,506,819	2,944,322
Gunpowder and other explosives...	67,887	868,728	1,888,741
India rubber, gutta percha, and manufactures of.....	88,816	1,090,367	2,364,157
Ink, printers' and other.....	.....	147,057	259,776
Leather	.....	11,175,141	15,363,584
Lime } Cement }	77,568	134,994	{ 85,854 / 163,162
Malt	.....	60,412	215,198
Malt liquors	42,664	654,408	2,137,527
Matches.....	153,680	52,284	95,316
Naval stores	9,799,923	7,444,446	12,474,194
Oil cake and oil cake meal	.... .	7,999,926	16,757,519
Oils, animal	1,975,972	1,686,643	718,997
" mineral, crude.....	2,220,268	6,744,235	7,364,162
" " refined or manufactured.....	30,502,312	51,403,089	68,246,949
" vegetable, corn	.....	.....	1,351,867
" " cotton-seed	146,135	5,291,178	14,127,538
" " linseed	23,770	55,036	54,148
" volatile or essential	248,270	223,435	256,597
" all other	.....	102,792	554,295
Paints, pigments, and colors.....	179,882	578,103	1,902,958
Paper and manufactures of	795,176	1,226,686	6,215,559
Paraffin and paraffin wax	.....	2,408,709	8,602,723
Perfumery and cosmetics.....	375,011	430,151	*358,589
Photographic materials	.....	3,891	1,164,465
Plaster	.....	5,153	35,017
Lard.....	22,429,485	33,455,520	41,939,157
Lard compound and substitutes....	.....	.....	1,474,464
Oleo and oleomargarine	.....	6,773,522	10,920,400
Butter.....	1,109,496	4,187,489	3,142,378
Cheese	12,270,083	8,591,042	4,939,255
Milk	.....	303,325	1,133,296
Salt.....	18,378	29,073	55,833
Soap.....	684,739	1,109,017	1,773,921
Spermaceti.....	35,915	116,757	67,125
Spirits, wood.....	.....	.....	320,306
" grain (neutral and cologne)	.....	178,257	59,277
" brandy	.....	.....	83,698
" rum	.....	663,039	903,808
" whiskey, bourbon.....	.....	498,250	764,860
" " rye	.....	137,029	121,241
" all other	.....	165,535	24,921
Starch	524,596	378,115	2,604,362

* 1899.

	1876.	1890.	1900.
Sugar and molasses	6,745,771	3,029,413	3,697,366
Tallow	6,734,378	5,242,158	4,398,204
Varnish	54,906	206,483	620,059
Vinegar	6,133	10,520	12,583
Wine	33,483	270,930	62,592
Wood pulp	.....	2,245	458,463
Yeast	.....	.....	36,061
	102,054,750	174,803,105	264,501,771

The figures show grand totals as follows :

For the year 1876	$102,054,750
" " " 1890	174,803,105
" " " 1900	264,501,771

In the decennial period just closing, the increase in the value of the exports of products of domestic manufacture was therefore about the same as during the preceding fourteen years, and during the quarter century the growth has been 260 per cent. The growth has been persistent and steady and indicates what may be expected in the immediate future as well as what is now the condition of development of our chemical industries. This latter condition becomes more manifest when we consider that the products exported constitute but a small proportion of the production, and we may in some degree at least anticipate the results which must be obtained in the pending census investigation.

As further illustration of the growth of the chemical industries, we may call attention to the condition of the coke industry in the United States in 1880 and 1898, respectively, as illustrated in the following table :

	1880.	1898.
Establishments	186	342
Ovens { built	12,372	48,447
Ovens { building	1,159	1,048
Coal used, net tons	5,237,471	25,249,570
Coke produced, net tons	3,338,300	16,047,299
Total value of coke at ovens	$6,631,267	$25,586,699
Value of coke at ovens, per net ton	$1.99	$1.594
Yield of coal in coke, per cent	63.0	63.6

If we consider that in the recovery ovens, which are fast taking the places of the older and less rational types, this coal should yield 3.38 per cent. of tar, 0.34 per cent. its weight of ammonia and 8.17 per cent. of gas liquor, all of them bases of most important chemical industries, the figures are significant.

Equally interesting must be the information to be furnished regarding the capital represented in the chemical industries in this country. At the present time, we are able to judge of this to a minor extent from the reported capitalization of the recently organized companies constituting combinations of preexisting companies. It is true that in these cases the capital represents in a very considerable measure what is known as good will, franchises, etc., but it nevertheless represents earning power and the average market value corresponds very closely with par value. Taking only those organizations devoted to the chemical manufactures exclusive of the gas and metallurgical and explosive industries, we find that the capitalization as reported in the stock lists amounts to the enormous value of about $1,500,000,000 and this takes no account of many of the incorporated industries not specially reported, nor the industries not incorporated and yet active. It does not include the recently developed electrolytic industries, in which the cash capital actually invested, as we learn from competent authority, amounts to more than $1,500,000. The newly established by-product coke industry is rapidly developing and is absorbing capital with wonderful rapidity, while the comparatively new beet-root sugar industry has already developed to such an extent as to involve capitalization of nearly $100,000,000 and to develop the establishment of manufacturing plants of magnitude beyond the imagination of foreign manufacturers in the same line a few years ago. Yet this is a general characteristic of the modern chemical industries of the United States and it is interesting to note that much of the development has been effected empirically and by men comparatively little versed in the principles and laws of the science upon which they are based. The industries have had the aid of but few educated chemists. Happily this condition is rapidly changing. Rational work is coming to be recognized and the demand for well-trained chemists is increasing. We cannot yet boast with the Germans that single works employ more than 100 thoroughly educated chemists, yet inquiry shows that many of the important works have corps of chemists numbering from 10 to 50, while very many more have smaller numbers. The same inquiry affords some clue to the number of chemists actually at work in this country. If we compare the list of members of the American

Chemical Society, we find that more than two-thirds are engaged in technical work. Furthermore, of the few chemists reported in the inquiry just referred to, scarcely one-third are members of the Society. A fair estimate based upon such data leads to the conclusion that more than 5,000 chemists are actually at work in the United States, and that 80 per cent. of these are connected with the industries. A study of the lists of the graduates of the educational institutions leads to similar conclusions. Fischer reported as the result of special inquiry made three years ago that in Germany 4,000 graduate chemists were employed in the industries and about 200 in teaching and special investigations.

So then we find that the chemical industries of the United States are growing with enormous rapidity; that they are being concentrated into fewer but larger works; that operations and reactions are being carried out with a magnitude which the earlier chemists would never have predicted; that new methods are being followed; new principles applied, greater accuracy of results demanded both as to quality and yield of the products; that the products now issue from the works in lots of tons at a time of a higher degree of purity and with a greater economy than was possible but a few years ago with lots of a few hundred pounds. For instance, the great sugar refineries each yield from 1,000,000 to 2,000,000 pounds daily of a product, the purity of which may be considered absolute. The modern beet-sugar works have in some cases capacity for treatment of from 1,000 to 3,000 tons of roots daily and consequently the purification of almost an equal quantity of juice.

And if so great advance has been made during the closing quarter century and even decade, what shall we say of the possibilities of the future? What is to be the magnitude of the chemical industries of the United States? What shall be the character of the products issuing from them? What will they require of the men who must direct and control them? That is to say, what will be the educational requirements of the American chemical industries of the almost immediate future? These questions are not new to our own country and their importance has forced itself with powerful intensity upon those engaged in the chemical industries in the old world; it has been the subject of most earnest discussion, particularly in Germany and England, during

the past five years at least. Nor has it been in all respects satisfactorily answered. Even within this closing month of the closing century the cable has flashed news of the complaint on the part of the leading statesmen of England that the training of technologists in that country is inadequate to the development necessary to meet foreign competition and at almost the same time brings news of the inauguration of new institutions for technical education. And in Germany also, the home and starting-point of many of the great industries, the demands upon the educational institutions for the better training of technologists are being pressed from every side. It is natural to believe that the time is not far distant when we too shall be called upon to make and meet similar demands. It may be pardonable therefore to discuss briefly what these requirements are likely to be.

First of all, experience shows that those who financially control the great industries, fully appreciate the need of improvement in both processes and products, are particularly apt in propounding hard questions in connection therewith and always expect that these questions shall be answered quickly and with the utmost accuracy. Young men who early come to a realization of this fact and prepare themselves by broad and thorough education to meet it are those who will succeed in the industries and ultimately have a controlling influence in their management. And what is to be said here on this subject is directed as much to the students as to those who instruct, for it is not difficult to understand the restrictions placed upon teachers by the students themselves, in the struggle to arrange work leading to the training, which many realize to be absolutely essential to meet the requirements of the near future.

For it is beyond question that the most thoroughly educated man is sure to best meet these requirements and become the leader in the industrial struggle of the near future. Dr. Duisberg, the director of the great color works at Elberfeld, Germany, rightly fixed the standard when he said that "above all a general comprehensive education is required. We must have in the industries persevering, energetic men with broad views." And Dr. Chittenden was right when he said: "Given a young man of broad knowledge and a thorough conception of the principal laws of physics, mechanics, hydraulics, etc., and he will soon adjust him-

self to the environment of professional work, and eventually rise to a plane far beyond that of the man whose training has been purely technical," and concluding his paper he says: "The rapid development of the sciences and their manifold industrial applications have opened up avenues for new ventures of great magnitude and there is an increasing demand for young men of broad scientific knowledge and training. He who wishes for the fullest possible measure of success must prepare himself thoroughly for his life work and he can do this in no better way than by acquiring a broad and liberal education."

This important requisite to success could not be better described. Careful general training is conducive to the best thought and the best expression of the results of inquiry. And it is too frequently true that technical men are especially lacking in this particular. Too early specialization must tend to narrowness of view, and therefore to limited influence. The general culture work of the preparatory schools or of the colleges will always be profitable, whether as preparatory to a specialty or an auxiliary to its prosecution. These principles will apply to all technologists whether they are chemists or not.

But what shall be the character of the special training of the technical chemist? First of all, we must admit, that this must cover thoroughly and profoundly a study of the science of *chemistry*. Dr. Fittig declares: "Our problem is to study the science as such; to lead the student into the methods of strictly scientific investigation, to put him into position to solve pure scientific problems entirely independent of the question, whether he shall devote his powers to the service of the science itself or apply it to practical questions." He claims that many students take up the study without the scientific instinct. And Erlenmeyer says: "A true scientific training should produce ability and susceptibility for all and every use. With a knowledge of the principles and laws of the science, their use becomes easy, they proceed independently." Foerster, discussing the needs of the electrochemists, says: "But above all be particular to secure fundamental training in the entire field of chemistry, thus utilizing the principle insisted upon by Liebig, that the best training for any specialty rests upon the broadest foundation in the whole of scientific chemistry." Dr. Duisberg says further: "In technical chem-

istry the sharp eye of the scientifically trained man is wanted in order to recognize the individual developments of the reactions in progress, which can be seen only through the accompanying indications." And Richard Meyer truthfully declared: "If our technologists did not properly appreciate the service rendered by men trained in the spirit of Liebig, chemical investigation would miss the stately crowd of auxiliary powers, without which the heights from which we may now look proudly backward and hopefully forward, could never have been attained." And W. H. Perkin says that "technical education will be of small value unless it is carried out on a very broad and scientific basis."

These views of the leaders in the science of chemistry must find an echo in the mind of every man who has had experience in the industries. In no department of human activity is a thorough knowledge of the fundamental laws so needful, nor can the knowledge of any law be safely neglected if successful work is to prevail. For all the laws apply all the time and few cases will arise in which the more important can be avoided. To suppose that the industries can be carried on in the face of severe competition without such knowledge is to invite failure in every case. Empiricism may succeed in times of plenty, but adversity breeds rationalism and fosters the support it can bring. So then we may make no distinction between inorganic and organic chemistry, analytic and physical chemistry, for each one has its place in the world's work, and no one can predict when any one of these branches will be called upon to render material aid.

But whatever may be the department of chemical study the relation of the science to physics will be keenly felt, and the dependence of each upon mathematics as the true foundation will become manifest. For this latter science is just as powerful an aid in the determination of the motions of the atom and molecule in matter as those of the worlds and constellations in space. And if it cannot be neglected in astronomy, no more can it in chemistry and physics. Indeed, it illustrates the unity of all the sciences, even as it does the correlation of all the forces. Dr. Lorenz set forth the need of all chemists in this particular when he said: "Modern electrochemistry is an exact science, and its principles, and a knowledge of it rests upon a foundation of mathematics. It is in every way desirable that every electro-

chemist shall be trained in the higher mathematics, and be thoroughly able to utilize both differential and integral calculus." He particularly recommends as a preparation therefor the "Introduction to the Mathematical Treatment of the Sciences" of Nernst and Schönflies and says: "If the student have an intensive rather than extensive training in mathematics, he may be thrown into the sea of natural science and left to swim." So also Foerster discussing the character of the instruction in electrochemistry in the technical high school, while insisting upon " thorough fundamental work in inorganic and organic chemistry, physics and physical chemistry" does not fail to include in his plan of work " the principles of higher mathematics." Dr. Koerner, discussing the importance of physical chemistry to the industries, says: " It is most characteristic of it (physical chemistry) that it utilizes the most powerful of all natural aids to scientific investigation, the higher mathematics." And in the curricula of the technical high schools in Germany we find almost without exception that in the course of chemistry, as well as in engineering, the higher mathematics is taken up and completed before the end of the first year, if not before the end of the first semester. It thus becomes the ground-work of and preparatory to, all the important work, which in those great institutions must follow it.

And finally, the technical chemist of the near future must be trained in the principles and practices of engineering, trained to make and operate the mechanical means for carrying out effectively the chemical reactions of the industries in a large way. For after all these reactions differ only in degree from those of the research and preparation laboratories, and if in the latter the students must be trained in making and assembling the forms of apparatus for use in the various operations of pulverizing, separating, roasting and incineration, solution, precipitation, separation of solids and liquids, washing, drying, and care of precipitates and crystals, the production and control of heat, the transfer of solids and liquids, the production and application of vacuum, evaporation and distillation, the conditions of crystallization, etc., in the small way in the laboratories, he must be taught to apply all these and more, in the large way in the works. Indeed, the only difference between the two may be comprised in the terms microchemistry and macrochemistry ; chemistry and the opera-

tions belonging to chemistry carried on in a small way with limited or small quantities or volumes; handling solids and liquids in quantities of a few grams or a few cubic centimeters or liters on the one hand, or of tons of solids and thousands of gallons of liquid on the other. How, for instance, would the chemist, untrained in the principles of engineering, proceed in handling materials in quantities involving several tons of solid matters and 30,000 to 50,000 gallons of liquid in a single charge, a requirement not uncommon in the modern industries and sure to be more common in the future industry. In his day, perhaps, the great Liebig was right, and Wöhler was right, and Fittig, not far wrong, when they maintained that with a thorough knowledge of the principles and laws of chemistry, all else in the industry involving their application would be easy. It is possible that the genius of the young operator would come to his aid and enable him ultimately to devise means to meet his ends, but time and labor must be saved by training in the methods, whereby such means may be established and a knowledge of means already at hand acquired. The authoress of a late popular work of fiction was right when she said "untrained genius is a terrible waste of power," and though it may not be as applicable here as in an earlier paragraph, she was also right when she said in the same connection, "So many persons think that if they have a spark of genius, they can do without culture; while really it is because they have a spark of genius that they ought to be and are worthy to be cultivated to the highest point." And this applies to the chemists who must operate in a large way and with large masses of matter, either solid or liquid.

In a discussion of this subject in England, where perhaps more than elsewhere in the world the need of engineering capacity on the part of chemists has been most keenly felt, and where on the other hand engineering capacity embodied in such men as Mond, Bell, Muspratt, Weldon, Perkin, and Chance, has brought forth such splendid results, Ivan Levinstein, himself, a leader in the industry, said: "It must also be palpable that a chemist intended for industrial work, who, along with sound training in chemistry, has also acquired a fair knowledge of chemical engineering, must be better fitted for his work than the man who is only practically acquainted with the handling of china basins, phials, or a Liebig's

condenser. And in the same discussion Watson Smith endorsed "what had been said as to the importance of teaching the scientific principles involved in the special construction of apparatus and plant for chemical processes on a large scale."

Dr. Ost, whose connection both with the industries and teaching, has been so intimate, says: "Liebig, who had for long years taught technical chemistry in Giessen and, as none other, had promoted the applications of chemistry, could say, in 1840, 'I know many (those trained in pure science only) who now stand at the head of soda, sulphuric acid, sugar and cyanide works, dyeing and other industries, and without ever having had previously to do with them, were completely entrusted with works' processes within the first half hour, and in the next brought forth a number of most important improvements.' Sixty years ago, this judgment characteristic of the time, this enthusiastic declaration of Liebig, would constitute a dogma, but it is no longer tenable. The chemist graduated from the technical high school is no longer in position to begin his factory experience with introduction of improvements." This, Ost says, is because of the better and more perfect organization of modern works. And Dr. Lorenz, of the Zurich Polytechnicum, says: "The electrochemist should not be graduated until he has been taught how to use modern methods in very large apparatus. We find in electrochemistry a wide difference between the theory and the facts. In the laboratory, current yield and greatest economy of electrical energy are often the principal considerations, but in technology corrosion of electrodes or diaphragms is much more expensive than any variation of energy." What an important illustration of a special study of materials of engineering in the preparation for the chemical industry! And what a sensation of sympathy this must arouse in all those who have had to do with the handling of corrosive materials in the very large quantities and volumes, which modern methods involve! How often it happens that success of an important operation is delayed and even made impracticable because of want of knowledge of suitable resistant material for construction of containing vessels or apparatus. Probably the most important contribution to this subject is that of Mr. Beilby. In his address he says: "I have rarely seen the chemistry of a process lagging behind the engineering; most frequently it is the

other way. The chemical reactions involved in the ammonia soda process are simple and easily understood, but it required the genius and practical skill of men like Solvay and Mond to devise apparatus which could establish the manufacture on its present secure basis. What are the elements of which the skill is made up? The scientific basis must be a thorough knowledge of the principles of chemistry, physics, dynamics, and mechanics, and added to this there must be a practical acquaintance with the materials of construction and the methods by which they are worked into structures. The designing and construction of apparatus for chemical works is a distinct branch of applied science. It is in this that special skill is required, for works' operations are not simply laboratory operations. The ideal chemical engineer should be in thorough sympathy with the modes of thought and with the methods of working of both the chemist and the engineer; just as the professor of engineering teaches how to apply the laws of statics, dynamics, and kinematics to the design of structures or machines, so should the professor of chemical engineering trace the applications of the laws of chemistry and physics and dynamics in the problems which occur in designing chemical apparatus for works. I am quite satisfied that in the present state of popular opinion the position and work of the technical chemist will not be properly recognized, unless he can associate himself, by his training and practice with the engineering side of his calling." Prof. Meldola says: "The sooner a chemist is made to realize the enormous practical difference between a laboratory and a factory process, the better it will be for him."

Prof. J. A. Reynolds, Director of the Municipal Technical Schools of Manchester, England, says: "English chemists are not engineers and English engineers are not chemists, and hence the enormous difficulty which arises in the endeavor to bring to successful commercial results the fruits of laboratory research." While Mr. David Howard considers that "the influence of mass action, the question of so many pounds of coal per horse power hour, and other like things, cannot be dealt with on a small scale, but are all important on a larger scale. We want chemical engineers who can make new roads in chemistry, as mechanical engineers do in railways."

It is also important to consider the course of study proposed by Mr. Beilby in his paper for prospective industrial chemists. His large experience in the chemical industry gives him power to speak with authority, and young men who look forward to a successful career in the industry, will do well to give it most careful consideration. And even more important, perhaps, are the courses of instruction carried out in the West of Scotland Technical College and in the Municipal Technical School in Manchester, England, and published in the Journal of the Society of Chemical Industry during 1899. Students who have had the advantage of these courses must be better fitted than those who have not been similarly favored. Yet we must believe that the courses laid out in the technical high schools of Germany and, we are proud to say, in some of the schools of technology in our own country, are in some respects better. Yet a combination of the two courses might be made with profit to both classes of institution. It is important that the works' chemists should be trained in the construction of the special forms of apparatus he needs to use, but they should be accompanied or preceded by the principles and practice of mechanical engineering. The most practical courses, perhaps, are those laid down in many of our own educational institutions for instruction in mining engineering and metallurgy, in which chemistry of the operations is considered in connection with the mechanical details of its applications, and we have advised students desiring to prepare for the chemical industries to pursue these courses in the best institutions first, and to follow them with a year or more of exclusive study of chemistry both pure and applied. If it were possible to add to the courses of chemistry as much of engineering, civil, mechanical and architectural, as is found in some of the metallurgical courses, the ideal would be more nearly met. But we can fully sympathize with those teachers who find the time available too limited for such a combination, and appreciate the fact that either the student must come to the professional school with better preliminary training in the preparatory subjects, or the courses must be extended beyond the usually provided four years' work. In any case, if a course of engineering could be carried side by side, and simultaneously with the course of chemistry, the needs of the prospective technical chemist would be

most fully met, and the requirements of the future chemical industry most nearly fulfilled. In some of our institutions in which all studies are practically optional, such a course might be arranged and profitably followed, and notwithstanding the longer time which might be involved in its completion, the graduate from it would issue with brighter and better prospects of success in his profession than one less broadly trained. And in the selection of the subjects for such a course, the plans of study laid down in the technical high schools of Germany, in the technical schools of England, and of our own country, may be profitably followed.

In 1897, we expressed the view which seems thoroughly applicable now and which will perhaps bear repetition here. We said: "It seems therefore that the demand of the present time, and of the immediate future can be met only by broadly educated men: by men who have been trained, not only in chemistry itself, but in the great principles of physics as well. A good technical chemist must be first of all a thoroughly educated chemist; after that, to attain the highest success in this country, he must be educated in the principles of engineering; the productions and applications of heat; the productions and applications of electricity; the transmission of power, the movement of liquids; in general, the means whereby the reactions of chemistry may be carried out in a large way. We need, therefore, chemical engineers and these in the nature of the requirements must be broadly and thoroughly educated men. While they must be trained in the work of the research laboratories, which are being organized in connection with many of the great industries, they must likewise be prepared to put into practical operation in a large way the results of the researches they have been called upon to make."

These truths have not changed, and if these conditions of education and training are fully met, the progress of our chemical industries must be greatly augmented, the science, must, by reaction, be actively advanced, and following the experience of our German confrères in the words of Meyer, we may look hopefully forward and in the near future proudly backward, to accomplishments greater than the world has ever known.

EIGHTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1900.

By F. W. Clarke.

Received January 8, 1901.

DURING the year 1900, fewer new determinations of atomic weight than usual, have appeared. The data are given in the following pages, together with Herzfeld's research upon calcium, which appeared three years ago. It was unfortunately published through an unusual channel, and was therefore overlooked at the time. Attention may also be called to the presidential address[1] of Professor Morley before the American Chemical Society, which is a valuable discussion of the probable accuracy of our knowledge as to the ratio between hydrogen and oxygen.

NITROGEN.

Dean's research[2] upon the atomic weight of nitrogen, which was noticed in abstract in the report for 1899, has now appeared in full. Weighed quantities of silver cyanide were dissolved in nitric acid, and the nitrate solutions were titrated with a standard solution of potassium bromide. As the latter was not absolutely pure its silver value was independently determined, and the titrations give therefore the quantity of silver proportional to the cyanide. The last experiment of the series was made by solution of the cyanide in sulphuric acid instead of the nitric acid previously used. Attempts to reduce silver cyanide in hydrogen gave unsatisfactory results, due to the formation of paracyanogen and silver carbide. The final data are subjoined.

	Weight AgCN.	Weight Ag.	Equivalent of CN.
	6.2671	5.0490	26.039
	17.60585	14.18496	26.026
	17.1049	13.7801	26.049
	17.9210	14.43881	26.030
	12.11215	9.75875	26.028
	14.6672	11.81727	26.029
Sum,	85.67820	69.02889	26.032

[1] This Journal, **22**, 51.

[2] *J. Chem. Soc.*, **77**, 117.

If C = 12.001, then N = 14.031, the value finally adopted. All weights were reduced to a vacuum standard.

Another determination of the atomic weight of nitrogen has also been announced by Scott.[1] From ammonium bromide he finds $NH_4Br = 97.996$. For the chloride, $NH_4Cl = 53.516$. The first value is lower than that found by Stas, the second is in agreement with Stas. The full paper will appear early in 1901.

CALCIUM.

The following determinations by Herzfeld,[2] made in 1897, were overlooked at the time, and are now recorded here for the sake of completeness. Calcium carbonate was prepared from the bicarbonate, and reduced to oxide by ignition at a temperature of from 1300° to 1400°.

Weight $CaCO_3$.	Weight CO_2.	Weight CaO.	Atomic weight Ca.
3.9772	1.7504	2.2268	39.687
2.3614	1.0396	1.3218	39.655
3.2966	1.4510	1.8456	39.677
			Mean, 39.673

Calculated with H = 1, C = 11.92, O = 15.879. With O = 16, Ca = 39.975.

IRON.

The determinations by Richards and Baxter[3] of the atomic weight of iron are based upon the reduction of pure Fe_2O_3 in a current of electrolytic hydrogen. Two series of results are given, representing ferric oxide prepared by two distinct methods. For details of manipulation the original paper must be consulted.

First Series.—Ferric oxide obtained by calcination of ferric hydroxide :

Weight Fe_2O_3.	Weight Fe.	Atomic weight Fe.
3.17485	2.22096	55.885
3.61235	2.52750	55.916
		Mean, 55.900

Second Series.—Ferric oxide obtained by calcination of ferric nitrate :

[1] *Proc. Chem. Soc.*, **16**, 205.
[2] *Ztschr. des Vereins für die Rübenzucker-Industrie*, **47**, Heft 497.
[3] *Ztschr. anorg. Chem.*, **23**, 245.

Weight Fe_2O_3.	Weight Fe.	Atomic weight Fe.
3.97557	2.78115	55.883
4.89655	3.42558	55.891
4.35955	3.04990	55.891
7.14115	4.99533	55.870
6.42021	4.49130	55.882
		Mean, 55.882

Mean of all seven determinations, 55.89, when O = 16. With H = 1, Fe = 55.47. All weights were reduced to a vacuum.

GADOLINIUM.

Atomic weight determined by Benedicks,[1] by synthesis of the sulphate from the oxide. Data as follows :

Weight oxide.	Weight sulphate.	Atomic weight gadolinium.
0.4308	0.7171	156.57
0.5675	0.9451	156.35
0.5726	0.9534	156.44
0.6785	1.1301	156.29
0.7399	1.2329	156.10
1.3253	2.2063	156.52
		Mean, 156.38

Calculated with O = 16, and S = 32. The final result agrees well with the determination by Bettendorf, who found Gd = 156.33.

THORIUM.

Atomic weight redetermined by Urbain.[2] The thoria was purified by conversion into the acetyl acetonate, which was crystallized from solution in chloroform. It was then converted into sulphate. The atomic weight determinations (with O = 16), were made by calcination of anhydrous $Th(SO_4)_2$. Data as follows :

Weight sulphate.	Weight ThO_2.	Atomic weight Th.
1.0925	0.6815	233.30
0.5926	0.3699	233.75
1.0230	0.6384	233.58

Calcination of the hydrous sulphate gave lower values, probably because the octohydrated salt used contained traces of the sulphate with 9 molecules of water.

[1] *Zischr. anorg. Chem.*, **22**, 393.
[2] *Ann. chim. phys.*, (7), **19**, 223.

MISCELLANEOUS NOTES.

Muthmann and Böhm[1] have prepared pure yttria by fractional precipitation with neutral potassium chromate. The final sample was practically pure, and gave a good atomic weight determination. 2.46585 grams sulphate yielded 1.19523 grams of oxide. Hence Yt = 88.97, when O = 16.

Samarium has been studied by Demarçay.[2] By synthesis of the sulphate he finds the atomic weight of the metal to range from 147.2 to 148.0, when O = 16. The higher values, about 150, obtained by other investigators, he attributes to the presence of other earths. In a second paper[3] he describes one of these earths, which is intermediate between samarium and gadolinium, with an atomic weight of the metal equal to 151, nearly. This, however, is only a rough approximation, as the oxide was not sufficiently pure for exact work.

The density of krypton has been carefully determined by Ladenburg and Krügel.[4] From it the atomic weight of the element becomes, in two experiments, 58.67 and 58.81, or 58.74 in the average.

Ramsay and Travers[5] give density determinations and atomic weights for the new gases of the atmosphere as follows:

	Density.	Atomic weight.
Helium	1.98	3.96
Neon	9.97	19.94
Argon	19.98	39.96
Krypton	40.88	81.76
Xenon	64.00	128.00

Metargon is abandoned, as non-existent. Why the value for krypton should diverge so widely from that found by Ladenburg and Krügel, is unexplained. It will be noticed that most of these gases fall between the halogens and the alkali metals in the periodic system, although argon is still slightly divergent from theory.

Mme. Curie has continued her studies upon radium,[6] which were referred to in the report for 1899. She now describes a

[1] *Ber. d. chem. Ges.*, **33**, 42.
[2] *Compt. rend.*, **130**, 1185.
[3] *Ibid.*, **130**, 1469.
[4] *Chem. News*, **81**, 205.
[5] *Ibid.*, **82**, 257.
[6] *Compt. rend.*, **131**, 382.

radiferous barium chloride in which the mixed metals have a mean atomic weight of 173.6 to 174. In this sample, judging from spectroscopic evidence, there was probably rather more radium than barium.

TABLE OF ATOMIC WEIGHTS.

The following table of atomic weights differs but little from that issued last year. First, your committee gives its own list, in two columns, representing both standards of value, H = 1, and O = 16. The only change here is in iron, due to the work of Richards and Baxter. Richards' table is unchanged, except in the same item. The table of the German Committee is that which was issued in January, 1901, as an insert to the first number of the *Berichte*.

	Clarke.			
	H = 1.	O = 16.	Richards.	German.
Aluminum	26.9	27.1	27.1	27.1
Antimony	119.5	120.4	120.0	120.
Argon	?	?	39.9?	39.9
Arsenic	74.45	75.0	75.0	75.
Barium	136.4	137.40	137.43	137.4
Bismuth	206.5	208.1	208.0	208.5
Boron	10.9	11.0	10.95	11.
Bromine	79.34	79.95	79.955	79.96
Cadmium	111.55	112.4	112.3	112.4
Caesium	131.9	132.9	132.9	133.
Calcium	39.8	40.1	40.1	40.
Carbon	11.9	12.0	12.001	12.00
Cerium	138.0	139.0	140.	140.
Chlorine	35.18	35.45	35.455	35.45
Chromium	51.7	52.1	52.14	52.1
Cobalt	68.55	59.00	59.00	59.
Columbium	93.0	93.7	94.	94.
Copper	63.1	63.6	63.60	63.6
Erbium	164.7	166.0	166.	166.
Fluorine	18.9	19.05	19.05	19.
Gadolinium	155.8	157.0	156.?	156.
Gallium	69.5	70.0	70.0	70.
Germanium	71.9	72.5	72.5	72.
Glucinum	9.0	9.1	9.1	9.1
Gold	195.7	197.2	197.3	197.2
Helium	?	?	4.0?	4.
Hydrogen	1.000	1.008	1.0075	1.01
Indium	113.1	114.0	114.	114.
Iodine	125.89	126.85	126.85	126.85
Iridium	191.7	193.1	193.0	193.
Iron	55.5	55.9	55.9	56.

	Clarke. H = 1.	Clarke. O = 16.	Richards.	German.
Krypton	....	....	....	81.8
Lanthanum	137.6	138.6	138.5	138.
Lead	205.36	206.92	206.92	206.9
Lithium	6.97	7.03	7.03	7.03
Magnesium	24.1	24.3	24.36	24.36
Manganese	54.6	55.0	55.02	55.
Mercury	198.50	200.0	200.0	200.3
Molybdenum	95.3	96.0	96.0	96.
Neodymium	142.5	143.6	143.6	143.6
Neon	...	....	....	20.
Nickel	58.25	58.70	58.70	58.7
Nitrogen	13.93	14.04	14.045	14.04
Osmium	189.6	191.0	190.8	191.
Oxygen	15.88	16.000	16.0000	16.00
Palladium	106.2	107.0	106.5	106.
Phosphorus	30.75	31.0	31.0	31.
Platinum	193.4	194.9	195.2	194.8
Potassium	38.82	39.11	39.140	39.15
Praseodymium	139.4	140.5	140.5	140.5
Rhodium	102.2	103.0	103.0	103.
Rubidium	84.75	85.4	85.44	85.4
Ruthenium	100.9	101.7	101.7	101.7
Samarium	149.2	150.3	150.0	150.
Scandium	43.8	44.1	44.	44.1
Selenium	78.6	79.2	79.2	79.1
Silicon	28.2	28.4	28.4	28.4
Silver	107.11	107.92	107.930	107.93
Sodium	22.88	23.05	23.050	23.05
Strontium	86.95	87.60	87.68	87.6
Sulphur	31.83	32.07	32.065	32.06
Tantalum	181.5	182.8	183.	183.
Tellurium	126.5	127.5?	127.5?	127.
Terbium	158.8	160.	160.	....
Thallium	202.61	204.15	204.15	204.1
Thorium	230.8	232.6	233.	232.5
Thulium	169.4	170.7	170.?	171.
Tin	118.1	119.0	119.0	118.5
Titanium	47.8	48.15	48.17	48.1
Tungsten	182.6	184.	184.4	184.
Uranium	237.8	239.6	240.	239.5
Vanadium	51.0	51.4	51.4	51.2
Xenon	....	....	....	128.
Ytterbium	171.9	173.2	173.	173.
Yttrium	88.3	89.0	89.0	89.
Zinc	64.9	65.4	65.40	65.4
Zirconium	89.7	90.4	90.5	90.7

[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE DETERMINATION OF PHOSPHATES IN POTABLE WATERS.

BY A. G. WOODMAN AND L. L. CAYVAN.

Received December 21, 1900.

THE estimation of phosphates is a part of the sanitary examination of waters which has been somewhat neglected in the past, doubtless because the ordinary methods of determination are quite tedious and because the exact significance to be attributed to the presence and amount of phosphates is a question still in abeyance. There can be no question, however, in consideration of the probable decomposition and oxidation of the organic phosphorus compounds in animal excretions, that an excessive amount of phosphates in a water, unless otherwise accounted for, is an indication of pollution. If then the amount could be estimated by a method sufficiently simple and rapid, enough data might readily be gathered to render the determination of much greater value than at present. Especially would this be true in comparing several waters from the same locality.

Repeated trials of methods which have been proposed have shown that there is none which is perfectly satisfactory for accurate and rapid work. The extremely small quantities of phosphate found even in polluted waters would seem to preclude the use of gravimetric methods. Such methods, however, have been used. Hehner,[1] and also Harvey,[2] concentrate a large quantity of the water and determine the phosphate gravimetrically as ammonium phosphomolybdate. All gravimetric methods are objectionable on account of the time required. Furthermore, not being very delicate, they necessitate considerable concentration, which, as will be shown later, almost invariably occasions a loss of phosphate. Phipson[3] precipitates the phosphate from a large volume of water by means of alum and an excess of ammonia, making the final precipitation with ammonium molybdate. The process is a long one and experiments with a more delicate method showed that the precipitation of the phosphate is not complete.

[1] *Analyst*, 4, 23; and 5, 135.
[2] *Ibid.*, (1880), 197.
[3] *Chem. News*, 56, 251.

On the whole, the colorimetric methods seem best adapted for the determination. Several such methods have been proposed, based on the color given to dilute phosphate solutions by ammonium molybdate in the presence of nitric acid. Lepierre[1] evaporates a liter of water, dehydrates the silica by repeated evaporations with nitric acid, ignites strongly, and filters. The phosphate in the filtrate is estimated colorimetrically by ammonium molybdate. Jolles and Neurath[2] use potassium molybdate instead of the ammonium salt, and Jolles[3] has applied the method to the determination of phosphoric acid in water, removing the silica from the residue obtained by the evaporation of a liter of water by ignition at 130° C. These methods are open to the same objections as the gravimetric methods, namely that by requiring the evaporation of large quantities of water they introduce serious liability to error and are too tedious to be of general use. Furthermore, the temperature at which the residue should be ignited to remove silica is a matter of importance, especially when dealing with small amounts. In view of these considerations it was deemed advisable to make a critical study of the colorimetric methods.

APPARATUS AND REAGENTS.

Ammonium Molybdate.—50 grams of the pure neutral salt were dissolved in a liter of distilled water.

Nitric Acid (sp. gr. 1.07).—Approximately one part of acid (sp. gr. 1.42) to five parts of water.

Standard Phosphate Solution.—0.5324 gram of pure crystallized sodium phosphate ($Na_2HPO_4.12H_2O$) was dissolved in freshly distilled water, 100 cc. of nitric acid (1.07) added, and the whole diluted to 1 liter. This solution is diluted to make the standards. One cc. = 0.0001 gram P_2O_5. The solution keeps without change for several months if preserved in well-stoppered bottles of hard glass; after a longer time it becomes slightly stronger, owing to the silica dissolved from the glass.

Standard Silica Solution.—About 5 grams of precipitated and washed silica were dissolved in an excess of sodium hydroxide made from metallic sodium. The solution was made faintly acid

[1] *Bull. Soc. Chim.*, 15, 1213 (1896).
[2] *Monatshefte*, 19, 5 (1898).
[3] *Archiv. f. Hygiene*, 34, 22 (1899).

with nitric acid, diluted to a definite volume, and the silica determined in an aliquot part. The standard solution was made by diluting this strong solution until 1 cc. = 0.001 gram SiO_2.

It was found that sodium or potassium molybdate offered no particular advantages over the ammonium salt. The color obtained was no more intense and was distinctly greener, which made the reading of the standards much more difficult. It was found also that for a given amount of the phosphate solution the depth of color and the rapidity with which it developed depended to a certain extent upon the quantity of reagents used. The best results were obtained by the use of 4 cc. of the ammonium molybdate solution and 2 cc. of the nitric acid.

For comparing the colors the ordinary Nessler tubes were used at first, but it was found that if tubes of too small diameter were used the colors were not easily read; if of too large diameter the delicacy of the reaction is considerably decreased. The tubes which have been found most satisfactory have a capacity of 100 cc. They are of hard, white glass, about 2.5 cm. in diameter and 24 cm. long to the 100 cc. mark. The color is a rather difficult one to read closely and for very accurate readings probably some form of colorimeter could be used to advantage. For any but the most refined work, however, it will be found amply sufficient to compare the tubes by a north light against a reflecting white surface, such as a pure white unglazed porcelain tile supported at an angle of about 40°. This procedure was followed in all this work, and was found most practical where a number of tubes are to be compared rapidly.

Using no greater precautions than those just described, the delicacy of the test is considerable. If care is taken to choose two tubes, identical in all respects, it is possible to detect 0.002 cc. of the standard phosphate solution in 50 cc. of water. If the tubes are heated to 60° C. 0.001 cc. can be read. The delicacy of the reaction is therefore sufficient to show the presence of 1 part of phosphate as P_2O_5 in 500,000,000 parts of water. On the other hand, comparatively large quantities of phosphate may be present in 50 cc. of water, without causing precipitation or turbidity on the addition of the reagents except after standing a considerable time. On account of the difficulty in matching the more intense colors no higher standard than 10 cc. of the standard

solution in 50 cc. of water is ever used, and it has been determined by direct experiment that a standard as high as this will not become turbid at room temperature for twelve or fifteen hours. The color of the phosphate standard is an additive property; it makes no difference, apparently, whether the higher standards are made up directly or by the addition of more of the standard solution to the lower standards.

The question of the permanency of the phosphate standards was one of the first ones investigated. Lepierre, in the article previously cited, stated that the phosphate standards can be preserved for several months without change. Careful comparison of a number of standards from day to day, however, showed that this was not strictly true. The change in some of the higher standards while slight was still distinctly noticeable when carefully observed, and in others, especially the lower ones, the color faded so much in two or three days that the standards were rendered useless. Nor was any other substance found giving the right color which was suitable for the preparation of permanent standards. The most satisfactory was a dilute solution of picric acid, which gave a yellowish green color very similar to the phosphate color. But it was found impossible to keep even these standards in glass tubes since the solvent action on the alkali of the glass was sufficient to form a slight amount of the alkali picrate, which has a more intense color than the picric acid itself; hence, the standards slowly increased in color. The attempt was therefore abandoned and fresh phosphate standards were used for all comparisons.

STUDY OF THE PHOSPHATE REACTION.

For a given volume of water and a definite amount of reagents the depth of the phosphate color is a function of two factors; namely, the amount of phosphate present and the temperature. To determine the exact effect of the latter for the conditions employed in this work, readings of various phosphate standards were made at different temperatures. Differing amounts of the standard solution were diluted to 50 cc., and, after the addition of the reagents, were heated gradually in a water-bath from 20° to 60° C. Readings were taken every 5°. If the reagents are added after heating, the colors are not so clear. The heating was

not carried beyond 60° because above this temperature the standards become cloudy and the higher standards tend to precipitate. The maximum color is given between 90° and 100°, but the tendency to precipitation renders the reading at this temperature impracticable. The most satisfactory colors are obtained at 20°–30°, practically at room temperature. A variation of a few degrees causes only a slight error. The results are given in the following table :

Amounts phosphate added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
6 cc.....	6.2	7.2	7.7	8.2	8.7	9.6	...	10.2
	6.2	7.2	7.8	8.3	8.7	10.2	10.4	10.7
	6.2	7.7	8.2	9.0	9.2	9.7	10.4	10.3
Average	6.2	7.3	7.6	8.5	9.0	9.8	10.4	10.5
5 cc.....	5.1	5.9	6.6	7.3	7.8	8.0	8.6	9.6
	5.1	5.3	6.1	7.2	7.9	8.4	8.6	9.4
	5.1	5.2	6.3	7.1	8.0	8.3	8.7	8.9
	5.1	5.6	6.6	7.0	7.8	8.5	8.6	9.2
Average	5.1	5.5	6.4	7.2	7.9	8.3	8.6	9.2
4 cc.....	4.1	4.7	5.1	5.4	6.4	6.6	6.9	7.1
	4.1	4.8	5.1	5.5	6.4	6.5	6.8	7.3
	4.1	4.8	5.1	5.5	6.4	6.6	7.0	7.4
Average	4.1	4.7	5.1	5.5	6.4	6.6	6.9	7.2
3 cc.....	3.1	3.4	3.9	4.5	5.1	5.7	5.8	6.2
	3.4	3.7	4.4	4.7	5.2	5.3	5.7	5.9
	3.2	3.7	3.9	4.3	4.9	5.4	5.5	6.2
Average	3.2	3.6	4.1	4.5	5.1	5.5	5.7	6.1
2 cc.....	2.2	2.5	2.7	2.9	3.1	3.4	3.6	3.9
	2.2	2.5	2.8	3.1	3.2	3.4	3.7	3.9
	2.4	2.6	2.9	3.0	3.3	3.4	3.5	3.9
Average	2.2	2.5	2.8	3.0	3.2	3.4	3.6	3.9
1 cc.....	1.1	1.2	1.4	1.5	1.5	1.7	1.9	1.9
	1.1	1.2	1.3	1.4	1.5	1.7	1.8	1.8
	1.1	1.2	1.4	1.5	1.5	1.5	1.7	2.0
Average	1.1	1.2	1.4	1.4	1.5	1.6	1.8	1.9
0.7 cc.....	0.75	0.80	0.85	0.95	1.1	1.2	1.25	1.27
	0.75	0.80	0.85	0.90	1.05	1.15	1.25	1.28
	0.75	0.80	0.83	0.95	1.05	1.15	1.20	1.25
Average	0.75	0.80	0.85	0.93	1.05	1.17	1.22	1.26

Amounts phosphate added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
0.5 cc.....	0.60	0.65	0.70	0.80	0.90	0.95	1.05	1.10
	0.60	0.60	0.65	0.75	0.85	0.90	0.95	0.95
	0.60	0.65	0.70	0.75	0.85	0.85	0.95	0.95
Average	0.60	0.65	0.70	0.77	0.87	0.90	0.98	1.01
0.4 cc.....	0.45	0.50	0.55	0.65	0.70	0.75	0.80	0.80
	0.45	0.55	0.55	0.57	0.60	0.65	0.70	0.70
	0.45	0.55	0.55	0.58	0.65	0.67	0.70	0.70
Average	0.45	0.53	0.55	0.60	0.65	0.68	0.72	0.72
0.3 cc.....	0.33	0.36	0.39	0.44	0.48	0.58	0.63	0.68
	0.33	0.36	0.39	0.45	0.50	0.55	0.60	0.65
	0.33	0.36	0.39	0.44	0.54	0.58	0.60	0.65
Average	0.33	0.36	0.39	0.44	0.51	0.57	0.61	0.66
0.2 cc.....	0.23	0.27	0.31	0.32	0.34	0.37	0.38	0.39
	0.23	0.27	0.30	0.33	0.33	0.36	0.38	0.39
	0.23	0.27	0.30	0.33	0.34	0.37	0.38	0.39
Average	0.23	0.27	0.30	0.33	0.34	0.37	0.38	0.39
0.1 cc.....	0.11	0.13	0.14	0.16	0.17	0.18	0.19	0.20
	0.12	0.13	0.14	0.16	0.17	0.18	0.19	0.20
Average	0.11	0.13	0.14	0.16	0.17	0.18	0.19	0.20

Some of the results are shown graphically in Fig. 1, in which readings have been taken as ordinates and temperatures as abscissas. The curves show slight irregularities, due to the difficulty of reading exactly. The increase in color with increased temperature is considerable, double in the higher standards. All of the standards on cooling go back to less than their original color. No case of precipitation occurred, although some of the highest standards were too turbid to be read easily.

Several of the methods previously proposed for the determination of phosphates involve the concentration of the water, followed by heating at various temperatures. Preliminary experiments had shown the liability to loss during such procedure, and the point was further investigated. One liter of water, containing 5 cc. of phosphate solution and 2 cc. of nitric acid, was evaporated to dryness; a loss of 16 per cent. of the phosphate occurred. Phosphate standards made up in a volume of 50 cc., with varying amounts of nitric acid, were evaporated to dryness and some of them heated in an air-bath at 100° for periods varying from

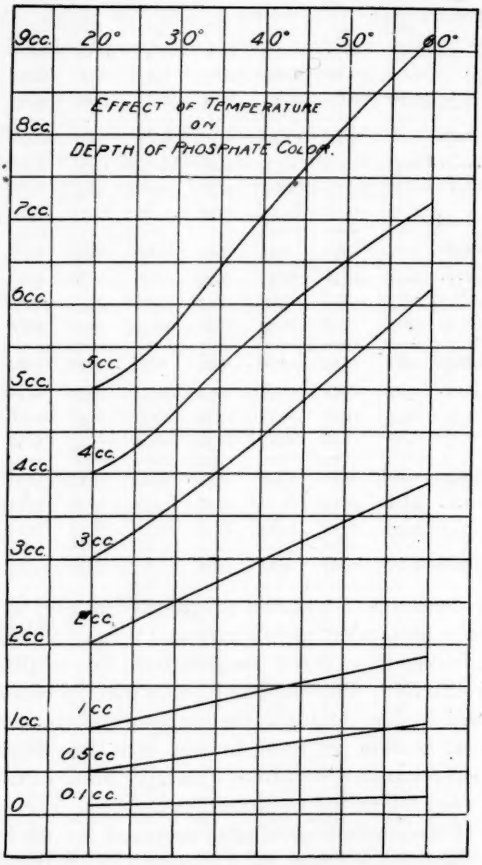


Fig. 1.

fifteen minutes to two hours. A loss of phosphate always occurred whether done in platinum or porcelain dishes. Other standards were evaporated and heated at 135° C., still others were ignited over a free flame ; a loss was found in all cases. An idea of the magnitude of the loss may be gained from the following figures :

EVAPORATED WITHOUT NITRIC ACID AND HEATED ONE HOUR AT 100°.

	In porcelain dishes.						In platinum dishes.					
Amount added	0.1	0.2	0.5	1.0	2.0	5.0	0.1	0.2	0.5	1.0	2.0	5.0
" found	0.1	0.18	0.45	0.75	1.8	4.9	0.07	0.12	0.4	0.85	1.8	4.9

EVAPORATED AS ABOVE BUT HEATED ONE HOUR AT 135°.

	In porcelain dishes.						In platinum dishes.					
Amount added	0.1	0.2	0.5	1.0	2.0	5.0	0.1	0.2	0.5	1.0	2.0	5.0
" found	0.0	0.0	0.0	1.0	1.5	4.0	0.0	0.0	0.1	0.6	1.3	2.7

In all cases where nitric acid was used and the residue was heated at 100°, the loss on a 2 cc. standard was from 0.02 to 0.22 cc. greater the more acid used. Where the ignition was made over a free flame the loss varied from 25 to 50 per cent., highest in the low standards. Without the addition of nitric acid the loss on evaporation was very irregular. In the presence of a definite quantity of acid the loss was more nearly constant. Without going into great detail it may be said that it was apparent that the loss was due to some change taking place while the solution is dilute and hot. The total loss occurs usually during the concentration of the solution to one-half its volume.

THE EFFECT OF SILICA.

The properties of dilute solutions of ammonium silicomolybdate were also studied since silica is the principal substance which interferes with the phosphate test.

Solutions made up with varying quantities of the standard silica solution gave a color immediately upon adding the reagents. With small and medium amounts of silica the color was slight compared with that developed in an hour; with high silica standards considerable color developed instantly. It is interesting to note that ammonium molybdate alone with a silica solution made exactly neutral, develops a faint color in an hour, but with a phosphate standard no color appears except in the presence of nitric acid. In twenty-four hours the color due to the silicomolybdate fades appreciably; it is greener than the color of the phosphomolybdate.

To determine the time necessary for silica standards to attain their maximum color varying standards were mixed with the reagents and 50 cc. of water and compared at definite intervals

with fresh phosphate standards. The readings in terms of the standard phosphate solution are given in the following table :

cc. SiO_2 used.	1/2 hour.	1 hour.	1.5 hours.	2.5 hours.	3 hours.	3.5 hours.
0.1.....	0.03	0.07	0.09	0.03	0.02	0.03
0.7.....	0.56	0.65	0.67	0.72	0.70	0.67
1.0.....	0.92	0.96	1.01	1.02	1.07	1.05
3.0.....	2.75	2.88	2.95	3.01	2.95	2.95
7.0.....	6.65	6.75	6.95	7.00	7.10	7.20
10.0.....	9.70	9.95	9.99	9.95	9.95	...

cc. SiO_2 used.	4.5 hours.	5 hours.	5.5 hours.	6 hours.	6.5 hours.	7 hours.
0.1.....	0.02	0.01	0.01	0.01	0.008	0.008
0.7.....	0.67	0.67	0.66	0.66	0.65	0.65
1.0.....	1.05	1.04	1.03	1.03	1.02	1.02
3.0.....	3.10	3.20	3.20	3.25	3.30	3.40
7.0.....	7.20	7.20	7.25	7.25	7.30	7.35
10.0.....	9.95	9.95	9.95	9.95	9.95	9.90

It will be noticed that the lower standards reach a maximum in about two or three hours, and then begin to fade ; the medium standards do not seem to reach a maximum even after seven hours.

A number of silica standards, after standing one hour, were heated from 20° to 100° in a water-bath. The color did not change in intensity until 70°–80° was reached, when it began to fade, decreasing up to 100°. The color did not return to its original intensity on cooling slowly to 20°.

Experiments made to determine the conditions under which minute quantities of silica might be rendered entirely insoluble, showed that evaporation with nitric acid and heating at 100° for an hour was insufficient ; when the same standards were evaporated and heated at 135° for an hour, recombination took place and some of the silica remained soluble. On heating the residues for *two* hours at 100° instead of one hour, however, no silica remained soluble. The results are shown in the following table : 1, 2, and 5 cc. of the standard silica solution were diluted to 50 cc., 10 drops of nitric acid were added, the solutions evaporated to dryness in porcelain dishes, and heated at different temperatures for two hours. The residue was taken up in cold water and the color read after standing one hour :

Temperature.	Readings.			Per cent. undehydrated SiO_2.		
	1 cc.	2 cc.	5 cc.	1 cc.	2 cc.	5 cc.
60°	0.5	1.2	2.0	50	60	40
80°	0.3	0.7	0.9	30	35	18
100°	0.0	0.0	0.0	00	00	00
135°	0.1	0.4	1.0	10	20	20
150°	0.4	0.5	1.1	40	25	22
190°	0.6	0.8	1.1	60	40	22

These results are shown graphically, using percentages of undehydrated silica as ordinates and temperatures as abscissas, in Fig. 2.

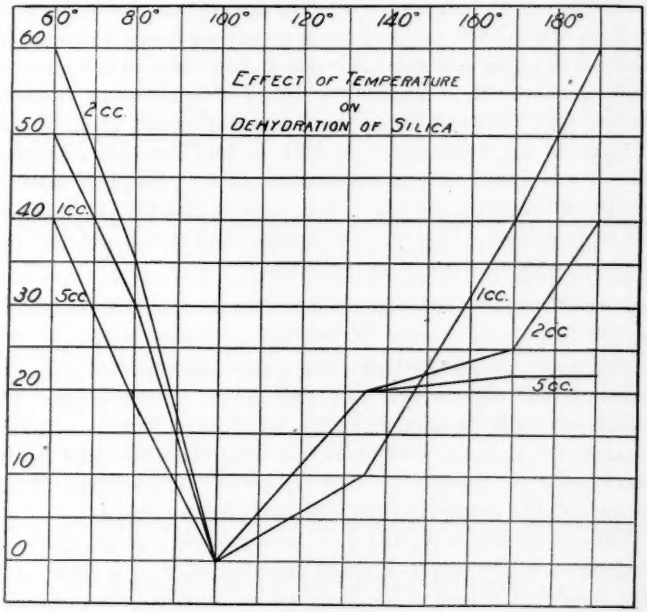


Fig. 2.

OTHER COMPOUNDS WHICH MIGHT INTERFERE.

Since vanadium and titanium resemble phosphorus and silicon quite closely in many of their properties, vanadates and titanates might interfere with the determination of phosphates by a colorimetric method. Titanium is especially liable to occur in the

natural waters of regions containing diorites and titanium-bearing ores like ilmenite. The presence of these elements has been observed in natural waters.

Dilute solutions of sodium titanate gave a pale greenish yellow color with ammonium molybdate and nitric acid, but much less intense than the phosphate color. The color did not fade within an hour, but at 20° C. it took twelve minutes for it to appear. By evaporation with nitric acid, and subsequent heating at 100° for two hours, the titanium oxide was rendered completely insoluble.

Ammonium vanadate gave with the ammonium molybdate *alone* a yellow color which was permanent for several hours, but upon the addition of nitric acid this color faded completely in five minutes. Experiments with a standard solution of ammonium vanadate showed that the color given by as much as 0.0003 gram of V_2O_5 in 50 cc. of water fades out entirely in four minutes. Incidentally it was found that 0.000001 gram of V_2O_5 could be detected readily in a volume of 50 cc. It is evident that the small quantities of vanadium which occur in natural waters will not interfere with the determination of phosphates.

COLORIMETRIC ESTIMATION OF PHOSPHATES IN THE PRESENCE OF SILICA.

The previous results had shown the possibility of a method based on the dehydration and elimination of the silica. The conditions must be such that the total phosphate or a definite portion of it shall be left intact and that the silica shall be rendered entirely insoluble. The following method was finally adopted as the one giving the most satisfactory results :

Fifty cc. of the water and 3 cc. of nitric acid (sp. gr. 1.07), are evaporated to dryness in a 3-inch porcelain dish on a water-bath. The residue is heated in an oven for two hours at the temperature of boiling water. The dry residue is then treated with 50 cc. of cold distilled water, added in several portions, and poured into the comparison tube. It is not necessary to filter the solution. Four cc. of ammonium molybdate and 2 cc. of nitric acid are added, the contents of the tube mixed, and the color compared after three minutes with standards made by diluting varying quantities of the standard phosphate solution to 50 cc., and

adding the reagents as above. A blank should always be made on the distilled water used for dilution, especially if it has stood for any length of time in glass vessels.

The method as just described will be sufficient for ordinary work. If a more exact determination of the phosphate is required a slight correction should be applied in each case. These corrections were determined by making a number of determinations by the method. The results are shown in the following table. The first two series had 2 cc. of standard silica solution added to each test; the others had only the phosphate.

Phosphate added.	Phosphate found.						Average.	Correction.
0.1	0.07	0.09	0.10	0.10	0.09	0.09	0.09	0.01
0.5	0.46	0.47	0.46	0.45	0.43	0.45	0.45	0.05
0.7	0.63	0.64	0.64	0.65	0.64	0.66	0.65	0.05
1.0	0.85	0.85	0.86	0.86	0.84	0.83	0.85	0.15
3.0	2.55	2.65	2.50	2.50	2.60	3.65	2.60	0.40
5.0	4.55	4.55	4.45	4.45	4.50	4.50	4.50	0.50
7.0	6.65	6.60	6.55	6.55	6.60	6.65	6.60	0.40
10.0	9.60	9.65	9.55	9.60	9.60	9.55	9.60	0.40

Since organic life is present in greater numbers and is more active in surface waters than in ground waters, it is evident that the determination will be of greatest value for the examination of wells. Well waters are usually colorless, and to them the method may be applied directly. It is not yet suitable for colored waters. The determination of phosphates is at present being carried on in this laboratory as a routine determination and the results will be published as soon as sufficient data have accumulated to render a discussion of the entire question of value.

BOSTON, MASS., December 20, 1900.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 54.]

EXPERIMENTS ON CHALCOPYRITE.

BY LEONARD P. MORGAN AND EDGAR F. SMITH.

Received December 6, 1900.

AT various times experiments have been made in this laboratory looking to the determination of the constitution of certain natural chemical products. Thus, the state of oxidation of the iron in pyrite, marcasite, and arsenopyrite has received

considerable attention, and in the present communication it is desired to give the results of similar experiments made upon the mineral chalcopyrite. Weighed portions of the latter were exposed in porcelain boats to the action of dry hydrochloric acid gas. As the mode of procedure has been sufficiently detailed in former papers, it may be omitted here. It will suffice to note that the heat was obtained from a single Bunsen burner with a wing top. The period of heating covered one hour, beginning of course with a gentle heat and increasing finally to a full red heat. The boat and contents were allowed to cool in the gas. On their withdrawal from the tube they were placed in a beaker containing distilled water. The combustion tube was also washed out carefully with water. The aqueous solution of the iron salt was strongly diluted, acidified with sulphuric acid and the liquid titrated with potassium permanganate.

RESULTS.

	Chalcopyrite. Gram.	Iron found. Gram.	Iron found. Per cent.
1	0.2112	0.06489	30.72
2	0.2039	0.06231	30.56
3	0.2007	0.06164	30.70
4	0.1996	0.06128	30.67
5	0.2089	0.06398	30.63
6	0.2140	0.06553	30.62

In several instances the liquid in the receiver placed at one end of the combustion tube showed traces of ferric iron when the thiocyanate test was applied. This might readily occur when it is remembered that the quantity of ferrous chloride thus volatilized was exceedingly small and that its exposure during the time required for the completion of the experiment would be enough to cause its oxidation. However, the quantity of ferric iron was extremely small.

The formula generally assigned the mineral is $CuFeS_2$, which would require 30.5 per cent. of iron. The results given above therefore indicate a complete decomposition of the material by hydrochloric acid, and also show that all of the iron is in the ferrous state. This proved to be the case with marcasite. As hydrochloric acid gas does sometimes act as a reducing agent, there was a possibility that perhaps it might have transformed any ferric iron present in the mineral into the ferrous condition.

To render the results as certain as possible, portions of the mineral were carefully heated in sealed tubes with a solution of copper sulphate, as had been done with marcasite. The evidence gathered in this way corroborated the first experience and it can safely be asserted that chalcopyrite contains all of its iron in the ferrous form, and that the mineral is, perhaps, nothing more than a substituted marcasite, in which copper has replaced its equivalent of iron.

UNIVERSITY OF PENNSYLVANIA.

ON TRIPHENYLCHLORMETHANE.

BY M. GOMBERG.

Received January 12, 1901.

THE recent publication by Norris and Sanders[1] on the same subject induces me to make a few remarks at this time. It is far from my intention to enter into any controversy whatever. I merely wish to call attention to the following few points :

(1) My paper on "Triphenylchlormethane"[2] was first presented by me at the Columbus Meeting of the American Association for the Advancement of Science, August, 1899. Norris and Sanders state that they have been at work on this subject for about a year. Hence this subject must have been undertaken by them after my paper was presented. It was, however, entirely natural that they should have overlooked the first mention of my paper, since it was given in the Proceedings[3] only by title.

(2) The difference in procedure between my method and that of Norris and Sanders consists in that the latter used, instead of benzene as a solvent, carbon disulphide,—a diluent first introduced by Anschütz[4] for Friedel and Crafts' reaction in general. The application of this solvent in the present instance enabled Norris and Sanders to isolate the important intermediate product, the double salt of aluminum chloride and triphenylchlormethane, which was not obtained by me at all.

(3) Norris and Sanders state[5] that the action of sodium upon triphenylchlormethane is entirely negative, even on two weeks'

[1] *Am. Chem. J.*, **25**, 54.
[2] This Journal, **22**, 752.
[3] Proceedings American Association for the Advancement of Science, **48**, 152 (1899).
[4] *Ann. Chem.* (Liebig), **235**, 341.
[5] *Loc. cit.*, p. 59.

contact in ether. Only on the addition of brombenzene to the above mixture did a reaction take place. One of the several products was a body free from halogen, yet on analysis the carbon and hydrogen did not add up to 100 per cent. The fact that "this compound resembles closely in melting-point, chemical composition, and solubility" the substance (the peroxide) described by me[1] shows that it is an oxygen body. One fails to see, however, how Norris and Sanders "discovered that an oxygen compound was formed as the result of the action of sodium on a mixture of triphenylchlormethane and brombenzene." No evidence is given that they excluded all oxygen-carrying reagents, such as sodium oxide, and that this was not the cause of the formation of that body, or that they worked in an atmosphere free from oxygen, and in this way established the non-formation of that body under these conditions. Furthermore, if the substance is really identical with the peroxide mentioned, it is not the result of the action of sodium upon a mixture of the two halogen compounds, but is formed by action of the atmospheric oxygen upon the unsaturated hydrocarbon (triphenylmethyl) which must have resulted in some way from the action of sodium upon triphenylchlormethane alone.[2] The reaction must, therefore, be analogous to that described by me for other metals: silver, zinc, and mercury. Only these three metals, in addition to the unsatisfactory results with sodium, are mentioned in my preliminary paper. Other metals, however, and different solvents, have also been tried and are being studied at present. Norris and Sanders now "propose to investigate the action of sodium on ethereal solutions of triphenylchlormethane of varying concentrations." I regret that having cleared up the difficult part of the problem (the action of metals upon triphenylhalogenmethanes) I am not to have, as it appears from Norris' publication, this field to myself for a while longer. It was stated[3] in my preliminary paper that only about two-thirds of the theoretical quantity of the unsaturated hydrocarbon is formed. The nature of the other products is being studied and I find that this varies according to the metal and solvent employed.

UNIVERSITY OF MICHIGAN, CHEMICAL LABORATORY,
January 9, 1901.

[1] This Journal, **22**, 762.

[2] Experiments show that small quantities of the triphenylmethyl *are* produced in this way.

[3] This Journal, **22**, 766.

SOLUBLE ARSENIOUS OXIDE IN PARIS GREEN.

PRELIMINARY REPORT.

By S. Avery and H. T. Beans.

Received October 30, 1900.

FOR the past six months, the authors of this article have been engaged in a more or less complete investigation of the arsenical insecticides, and while working with Paris green devoted considerable time to the study of the so-called "soluble or free arsenious oxide," and methods for its determination.

The recent appearance of two articles in this Journal, giving results somewhat different from those obtained by us, has induced us to present some phases of our work in this preliminary report.

Briefly, so much of these articles as has to do with the subject under consideration may be summed up as follows:

In his work on Paris green, J. K. Haywood[1] tried three methods for the determination of soluble arsenic.

1. A quantity of Paris green was weighed on a filter and extracted with cold water. Arsenic trioxide was found in the filtrate after 2 liters of water had been used and the method was abandoned.

2. Portions of 1 gram each were suspended in 500 cc. of water in stoppered flasks and the arsenic trioxide in solution determined every few days. The following table of results is given:

		Time in days.	Arsenic trioxide extracted. Per cent.
Paris green	A	2	1.01
" "		4	1.68
" "		8	2.69
" "		11	4.02
" "		14	4.02
" "	B	9	3.41
" "		12	4.86
" "		14	4.86

The author says, "It will be seen that this method finally gave constant and very likely correct results."

3. Extraction with water kept at 50° to 60°. The solution was filtered off and replaced by fresh water each day.

[1] This Journal, **22**, 768.

Time in days.	Total arsenic trioxide extracted. Per cent.
1	3.41
2	5.55
3	7.11
4	8.28
5	9.54
6	11.10
7	Still gaining

Since publishing the above, Haywood[1] has observed that in applying the second method above, some copper is obtained in the filtrate, indicating either the solubility of Paris green in cold water or its decomposition by that medium. He favors the former view, and to increase the accuracy of the method, determines the copper in solution and deducts the corresponding amount of arsenic trioxide from the total arsenic trioxide in the solution.

"It is of course possible, even probable," he says, "that the arsenious and copper oxides of Paris green do not go into solution in water in the same proportion that they are present in the original compound, but in the present state of our knowledge it seems to be the most plausible assumption that they do."

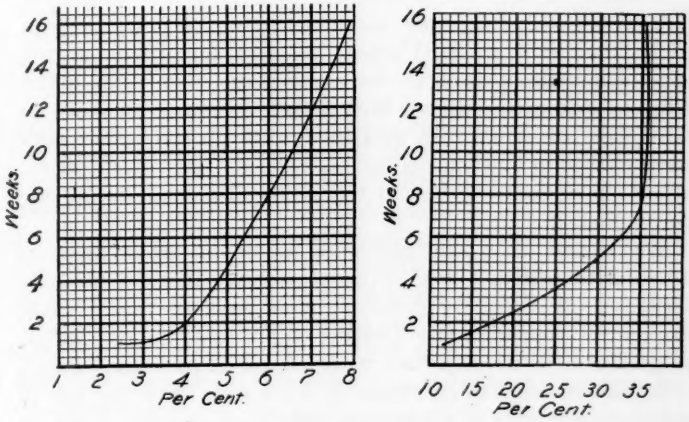
The second article mentioned is one by E. W. Hilgard.[2] The author states that a correction based upon the amount of copper in solution cannot be made since the copper and arsenic do not dissolve in the same proportion in which they are present in the original substance. As an illustration he gives an experiment in which cold water was allowed to slowly percolate through a sample of Paris green. After the passage of 2 liters there was no reaction for copper, though the arsenic continued to be extracted even after the fifth liter. No crystals of arsenic trioxide could be detected by the microscope in the residue thus washed, but only fragments of crushed globules.

In our work on the subject we used a large number of samples. Several samples of Paris green were made in the laboratory as well as other members of the series containing formic, propionic, and butyric acids, respectively, instead of acetic acid. We studied these as well as many commercial samples of Paris green. We shall confine this report, however, to experiments with one sample which we believe to be nearly pure for the reasons: (1) The

[1] This Journal, **22**, 705.
[2] *Ibid.*, **22**, 690.

analysis showed the percentages of cupric oxide and of arsenic trioxide to be nearly in the proportions required by Ehrmann's formula. (2) By treatment with boiling sodium acetate solution according to the method given later in this paper, less than 1 per cent. of arsenic was extracted. (3) The most careful microscopic examination failed to disclose anything but bright spheres of Paris green. (4) The unground sample on standing with water gave off soluble arsenic at a slower rate than any other sample that we have examined.

The sample was divided into two portions: Sample "A" was left in the original condition. In Sample "B" the granules of



Paris green were broken by grinding in a mortar. Several lots of 0.5 gram were weighed from each of these samples and suspended in 500 cc. of distilled water contained in tightly stoppered cylinders. At the end of every two weeks, 250 cc. of the solution were filtered off and titrated with standard iodine. The results of this experiment are plotted in two curves here given, in which the time in weeks is given as ordinates and the percentage of arsenious oxide in solution as abscissas. Owing to the marked difference in the rate of solution, the two curves are not drawn to the same scale.

In Curve "B" there is a gradual increase in soluble arsenic trioxide up to about the end of eight weeks when 35 per

cent. is reached. Beyond this time the increase is slight, being only 0.14 per cent. from the twelfth to the sixteenth week. At this time there was found in the filtrate 5.98 per cent. cupric oxide probably as copper acetate.

Had the copper and arsenious oxides gone into solution in the proportion in which they were present in the original sample, there should have been 19.57 per cent. cupric oxide instead of 5.98 per cent. in solution. It might be urged that the excess of arsenic over copper might be due to uncombined arsenic trioxide in the sample. Such an assumption would require at least 25 per cent. of uncombined arsenic trioxide.

While our results are in harmony with Hilgard's conclusion that copper and arsenic do not dissolve in the proportions in which they exist in Paris green, no close comparison of the experiments can be made as the experiments were made under different conditions. In our work all the products remained in the sphere of action. In Hilgard's work all soluble products were allowed to filter out as fast as formed. His green seems, also, to have been exposed to the action of the air during the percolation.

We believe that the action of water on Paris green is a hydrolytic action. Leaving out of consideration the probable formation of secondary products, it is probable that a small amount of copper acetate (whence the soluble cupric oxide), soluble arsenic trioxide, and basic copper acetate are formed. The reaction seems to take place in accordance with the law of mass action, a state of equilibrium being reached when about 36 per cent. of arsenic trioxide has passed into solution under the conditions previously stated. It is quite likely that all the arsenic could be rendered soluble by replacing the supernatant liquid with fresh water from time to time and allowing to stand for a longer period. In addition to the evidence already cited in support of this view it may also be added that the analysis of one residue showed 42.92 per cent. cupric oxide. The analysis of another showed 50.61 per cent. cupric oxide. This would be in harmony with the assumption of an increasing amount of basic acetate in the residues as the arsenic goes into solution.

We do not wish to lay any great stress on the probable nature of the products of the hydrolysis. We do, however, assert that

all samples of Paris green that we have examined (some of them nearly pure so far as can be determined by all known tests) are decomposed into soluble arsenic; that we have extracted 36.79 per cent. (considerably over one-half) of arsenious oxide from a sample which we have every reason to believe was practically pure, and that in all cases examined the per cent. of copper in the residue increases as the arsenic passes into solution.

It is, of course, reasonable to suppose that the same kind of action takes place with the unground sample, only much more slowly. The Curve "A" shows plainly that the condition of equilibrium has not yet been reached and probably the arsenious oxide would go into solution till the maximum quantity of about 36 per cent. had been reached.

From these experiments it would seem that, while a fair approximation to correct results may be obtained in some cases by suspending Paris green in 1000 parts of water and allowing to stand for a week, the method is quite arbitrary. In none of our work have we noticed any marked change in the rate of solubility at any particular time. On the contrary, the amount of arsenic trioxide in solution appears to depend almost entirely on the length of time of action, the concentration of the solution, and the state of division of the particles of Paris green. To obviate the above difficulties as far as possible, we have used a strong solution of sodium acetate instead of water. The use of such a solution has two advantages. In the first place, arsenic trioxide is much more readily soluble in a solution of sodium acetate than in water, hence much less time is required and consequently there is much less liability to decompose the Paris green.

Of much more importance, however, is the fact that the presence of sodium acetate in the solution largely prevents the hydrolyzing action of water on the compound, thus giving a somewhat sharper distinction between free arsenic trioxide and arsenic trioxide rendered free by hydrolytic action. While we believe this method better than the one in common use, it still leaves much to be desired.

For the determination we digest over the open flame 1 gram of the Paris green for about five minutes with 25 cc. of a solution of sodium acetate containing 12.5 grams of the crystallized salt.

The solution is then cooled, made up to 100 cc. and 50 cc. filtered off and titrated with standard iodine in the usual way.

In connection with this series of experiments, we tried the action of carbon dioxide on Paris green suspended in water. One gram of Paris green from the same sample as was used in the previous experiments and in its original condition, *i. e.*, not pulverized, was suspended in 500 cc. of water for one week, the water being kept saturated with pure carbon dioxide. At the end of this time the arsenic trioxide in solution amounted to 27 per cent. of the weight of the Paris green taken, or 48.5 per cent. of the total arsenic trioxide present had dissolved. There was also a little copper in solution, but this was not determined. The color of the residue changed from a bright green to a dull earthy color, some particles becoming nearly black. Had the sample been pulverized, the decomposition would probably have been practically complete.

As the result of our work, it seems to us that too much importance is being attached to the content of "soluble arsenious oxide" in Paris green. In the first place, since Paris green is of no very definite composition, and since water so easily hydrolyzes it into its constituents, the analytical results for "soluble arsenic" are uncertain and quite dependent on the conditions of the determination. In the usual method of analysis there is no method of distinguishing between the amount of "free arsenic trioxide" and "arsenic trioxide rendered free by hydrolysis." The extent of the hydrolysis is determined mainly by the length of time the water is in contact with the Paris green, and the state of division of the particles. This latter factor exerts by far the greater influence and is wholly beyond the control of the analyst. While the size of the spherical granules is fairly constant in any one sample, different samples show the widest variation. Aside from this variation in the particles themselves, nearly all samples contain a considerable proportion of broken granules of varying degrees of fineness.

Hilgard and others give 4 per cent. as the maximum amount of soluble arsenic trioxide a Paris green should contain if it is to be used for spraying purposes. The purest sample we have obtained gave 2.61 per cent. after standing in water for one week and 4 per cent. at the end of two weeks. A portion from the

sample after being ground was treated in the same way, giving 10.55 per cent. in one week and 17.51 per cent. at the end of two weeks, thus showing both the limitations of the present method of analysis and the marked influence of the state of division on the results.

In view of the fact that carbon dioxide, in the presence of water, so readily decomposes Paris green converting at least one-half of the arsenic trioxide into the soluble condition, it would seem that even if an absolutely pure sample were used in spraying, it might easily happen that the carbon dioxide and water-vapor of the air would convert much more than the limiting 4 per cent. arsenic trioxide into the free state. Probably many of the irregularities observed in the action of Paris green on foliage could be directly traced to weather conditions which happen to be favorable to the formation of free arsenic trioxide from a comparatively pure sample of Paris green.

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NEW BOOKS.

GRUNDZÜGE DER SIDEROLOGIE. VON HANNS FREIHERR V. JÜPTNER. ERSTER TEIL; DIE KONSTITUTION DER EISENLEGIERUNGEN UND SCHLACKEN. Leipzig: Verlag von Arthur Felix. 1900. Price, 13 M.

The author of this interesting and valuable work contends that the science of iron, while still far from mature, as we all know, has now become old enough to have a name of its own, and he proposes to call it "Siderology." This name is to be applied to that science which concerns itself not only with the intimate morphological and chemical constitution of iron alloys, but also seeks to determine in what ways these alloys or compounds are affected by outward influences, such as mechanical and heat treatment, and what connection exists between them and the physical and mechanical properties of iron and steel. In the author's view, metallography (Osmond) or siderography (Jüptner) bears the same relation to the science of siderology as petrography bears to the science of geology.

The work is to appear in three parts, of which the present volume of 315 pages is Part First. It covers theory of solution, micrography, the chemical constitution of iron alloys, and the chemical constitution of slags. The second part will treat of the

relation between chemical constitution, mechanical treatment, microscopic structure, and other properties of iron and steel. The third part will treat of the reactions between metal, slags, and other agents. The first 62 pages on "Theory of Solution" constitute a valuable scientific introduction to the study of iron alloys. In the chapter on micrography the methods of preparing and examining iron and steel under the microscope are given, with illustrations. Nearly all the more important work on those microscopic constituents of iron and steel which have been isolated, or otherwise identified, is here brought together in compact and convenient form. The author falls into an error, however, when he states that titanium appears to occur as such dissolved in iron. In pig-iron it is known to occur, and has been separated from it, combined with carbon as TiC in microscopic, cubical crystals.

The work closes with many valuable and probably fairly complete references to larger works and scattered papers on theory of solution, micrography, chemical constitution of iron alloys, and constitution of slags. P. W. SHIMER.

LEHRBUCH DER ANORGANISCHEN CHEMIE. VON PROF. DR. H. ERDMAN. Zweite Auflage, mit 287 Abbildungen, einer rechen Tafel und sechs farbigen Tafeln. Braunschweig: F. Vieweg & Sohn. 8vo. xxvi + 758 pp. Price, 16 M.

A great many topics have been well handled and some of them quite fully treated. The tables of spectra of the "Edelgase," xenon, krypton, argon, neon, and helium, are beautiful pieces of work. The description of the separation of these gases and the liquefaction of air and kindred topics occupy considerable space; the author enlarges on electrolytic dissociation, the ions, osmotic pressure, and kindred topics.

Less fortunate is the treatment of subjects belonging to chemical technology, which are, in a few cases, very badly handled.

No references are given to original memoirs. The synonyms are very fully given. In many cases the Russian name is printed and its pronunciation (in italic type) as well. The illustrations and the mechanical execution are up to the high standard so long maintained by this famous publishing house. E. H.